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Title of Proposed Research:

Assembly of Photosynthetic Antenna Protein / Pigments Complexes from Algae and Plants for Development of Nanobiodevices

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I. Abstract of the project results

Abstract

The purpose of this proposal is to use photosynthetic antenna pigment complexes from algae and plants as well as from photosynthetic bacteria in order to control the direction and orientation of the complex on electrodes with pattern for developing nanobiodevices (nanobiophotonics). The advantage of these pigment complexes from algae and plants as well as from photosynthetic bacteria is its high efficiency of light-energy conversion throughout the near UV to near IR region and much higher durability using these methods than ordinary light-harvesting (LH) complex isolated from photosynthetic bacteria. The present generations of sensor and semiconductor devices with an integrated circuit for developing nano-level size are too expensive to be cost-effective compared to other existing technologies. Expanding existing silicon device technologies and nanofabrication technics by incorporation of modified photosynthetic protein / pigments complexes or their protein-mimic materials to perform tasks of light-harvesting and charge separation, is currently explored as a novel concept, which makes use of natural protein environments to create a directional flow of light energy and electronic charge separation, meanwhile reducing the cost aspect by the use of bio-materials and their synthetic protein-mimic materials. The majority of the aim is construction of the array of artificial photosynthetic antenna system with nano-patterning substrate using modified photosynthetic protein materials prepared from modern biosynthetic manufacturing methods and photosynthetic pigments for developing nano-biophotonics as well as for energy harvesting materials.

We proposed a scenario where the construction of artificial photosynthetic systems with patterning substrate is expected to start from molecular and supra-molecular entities in a variety of smart matrices that collect light energy and separate charge for developing new types of nano-biodevices.

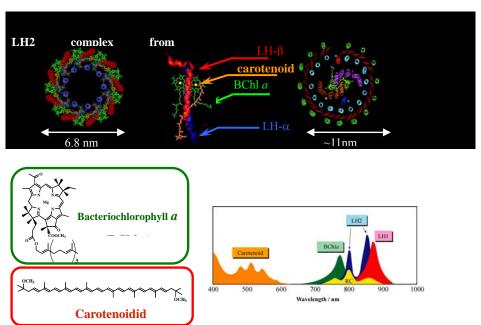
II. Result of the project.

1. Introduction

Nature provides a number of examples, in which processes of energy conversion, storage and transport are combined and optimized through 'smart matrices' at various levels, going from molecular to cellular or higher organisms. Based on biological design principles, future biology-based photonics or their synthetic organic photonics could form clean and inexpensive future alternatives for productions of nano-sensors and nano-semiconductors.

The past 10 years have seen tremendous progress in our understanding of the structure and function of the pigment-protein complexes involved in the primary reactions of bacterial photosynthesis. The structure of the reaction center (RC, the first membrane protein to have its structure determined to high resolution) revealed the nearly C₂ symmetrical arrangement of the redox centers and this system has now been extensively studied by ultrafast laser spectroscopy. More recently the structures of the LH2 complexes has revealed the nonameric and octameric arrangement of repeating units consisting of two apoproteins and

one or two carotenoids and three BChls while the recent crystal structure of the LH1-RC core complex reveals that the LH1 complex surrounds the contours of the RC although a high-resolution structure has not yet been determined for the LH1 complex (Scheme 1).



Scheme 1. Compartimentalization of light -harvesting and charge separation.

The antenna complexes(LH2,LH1-RC) efficiently realize various photosynthetic functions using cofactors (BChl a and carotenoid) assembled into the apoproteins (LH1 and LH2).

The light-harvesting mechanisms in these light-harvesting complexes have been studied both spectroscopically and theoretically. These advances put us in a unique position of being able to exploit this information to design artificial photosynthetic antenna systems based on 'biological blueprint'. Our aim is to see if we could produce an antenna module, which acts as a 'sensitizer', and a light-induced redox component for nano-biophotonics. As well as using LH2 and LH1-RC from photosynthetic bacteria (Scheme 1) this summary also propose to use photosynthetic pigment complex from algae and plants (Scheme 2) or their model complexes as a light harvester of the well-established cell. One of its unique features is that it works over a large dynamic range of incident light intensities. It has a remarkable ability to capture efficiently photons even at very low light fluxes, yet at the same time to withstand very high light fluxes by efficiently dissipating the excess photons. Thereby protecting itself against the potential harmful effects of over-excitation.

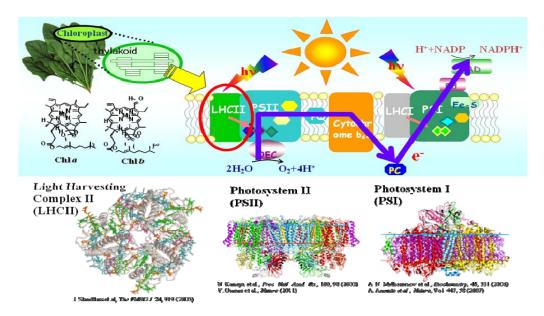
It is important to understand not only the mechanisms of efficient light-harvesting but also those of photo-protection. In order to understand these reactions both structural and functional information is required. The data on how the energy levels and intermolecular interactions of the pigments affect their energy-transfer properties, and how the 'durability' of the complexes is required for rational design of novel biophotonics. Based on the experiments using the native photosynthetic antenna complexes, a variety of modified complexes will be synthesized and tested for their usefulness in artificial nano-biophotonics. After

elucidation of the mechanisms of harvesting, transferring, usage and dissipation of light energy, our aim is to optimize under a given light intensity the energy-conversion efficiency and the durability of the core and the antenna complexes by modifying the pigment Cars and BChls or chlorophylls as well as the supporting peptides. These modified photosynthetic protein-mimic complexes was introduced into a membrane system on electrodes with pattern as a light-induced redox component, and the antenna complexes was attached to electrodes modified with or without lipid bilayers as a UV and Vis light harvester modules to produce a new type of nanobiophotonics. These approaches provided a foundation for using the artificial domains of photosynthetic core-antenna and antenna complexes with patterning substrate and the development of new type of nano-sensors and nano-semiconductors.

Approach

The present generations of sensor and semiconductor devices with an integrated circuit for developing nano-level size are too expensive to be cost-effective compared to other existing technologies. Hence there is a need for productions of sensors and semiconductors using novel-low-cost, systems with the inherently high photon-capturing and charge separation efficiency of natural photosynthetic systems. Integration of photosynthetic proteins or it pigments complexes with nano-patterned devices for tasks of light-harvesting and charge separation will expand existing silicon device technologies and nano-fabrication technics using novel and inexpensive bio-components. Design principles of natural photosynthetic units will form the guideposts for the design and development of native light-harvesting and photoconversion matrix modules as described in the section of a plan of work bellow. A critical step is creating functional supra-molecular nano-assembly of small organic building blocks that co-operate to create a directional flow of energy and electron using the operational principles of the natural systems. Properties of the building-block molecules intrinsically have the capacities to direct their co-operative assembly into structures with specific orientation and alignment. The advantages of the large scale of modern biosynthetic manufacturing methods offers a promising route to economically viable devices.

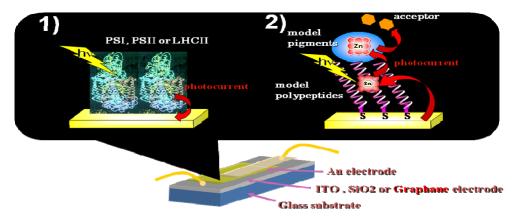
Our goal is to use photosynthetic pigment complex, FCP from algae, LHCII from plants, and PSII and PSI from algae or plants (Scheme 2 for plants) as well as LH2 and LH1-RC from photosynthetic bacteria (Scheme 1) or their model complexes as a light harvester of the well-established cell to convert light energy in the ultraviolet and visible region into that in the near infrared region for development of new type of nano-sensors and nano-semiconductors (nano-biophotonics). The advantage of the light-harvesting complex is its efficient capture of photons throughout the near UV to near IR region and much higher durability than ordinary isolated dyes supported by its inherent photo-protective function. Thus, the results of the above grounds can be directly applied to the development of nano-photosensors and nano-semiconductors using modified photosynthetic pigments or their model light-harvesting materials with nano-patterning substrate.



Scheme 2. Compartimentalization of light harvesting (LHCII) and charge separation (PSII &PSI). The antenna complexes (LHCII, PSII and PSI) efficiently realize various photosynthetic functions using cofactors (Chl *a* and carotenoids) assembled into the apoproteins.

In the current of our previous study, LH1 polypeptides with cysteine group or His-tag at the C- or N-terminal, analogous to the native LH polypeptide from photosynthetic bacteria has been assembled on Au or ITO electrode. In this study, pigments such as native and chlorophyll or carotenoid derivatives were further selected and assembled on the specific site of these polypeptides to control the organization of PSI PSII and LHCII (Scheme 3) which were more stable than the LH-RC or RC complex from photosynthetic bacteria and their model complexes on electrodes modified with or without lipid bilayers. The structural effects of the pigments and the polypeptides on the production of the efficient electron flows were examined.

Further, molecular assembly of porphyrin and carotenoid model pigments on electrodes using synthetic hydrophobic model polypeptide which have similar amino acid sequences to the hydrophobic core in the native photosynthetic antenna light-harvesting polypeptides, PSI, PSII and LHCII (Scheme 3) was achieved. This method was useful for the self-assembly of these complexes in order to study the energy transfer and electron transfer reactions (capture of photons) between individual pigments in the supra-molecular complexes on the electrodes with pattern for developing nano-biodevices.



Scheme 3 Artificial domains of photosynthetic pigment complex on various electrodes: Schematic model of the assembly of PSI, PSII and LHCII and their model complexes on an electrode

2. Experiment

More details are presented in our papers in the list of publication and in the abstracts of some representative papers attached.

3. Results and Discussion

1. Artificial domains of FCP and LHCII as well as LH2 and LH1-RC with nanopatterning substrate for development of antenna-mimics nano-photosensors, allowing them to work under dim or diffuse light

Molecular self-assembly of photosynthetic pigment complex as shown in Schemes 1 & 2 and their model complexes onto various electrodes was used to develop new types of antenna-mimics nano-sensors. In the current of our previous study, we used modified photosynthetic antenna complex with His-tag or modifiers at the LH polypeptide with SH using molecular biological methods to control the orientation and direction of the complex onto electrodes as shown in Scheme 4.

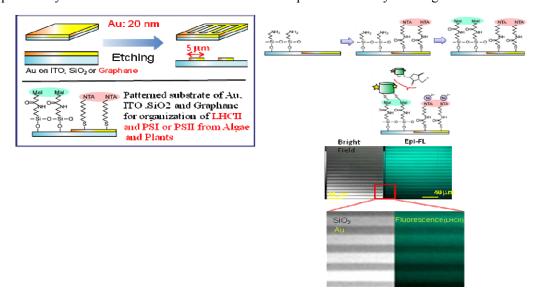
Task 1: Artificial assembly LH2 & LH1-RC with nano-patterning substrate to construct an efficient energy and electron transfer systems analogous to photosynthetic antenna complexes (Ref. 1 & 8: Biomacromolecules, 12, 2850-2858 (2011) & Biomacromolecules, 13, 432–438 (2012))

The pigment-protein complexes of the modified photosynthetic pigment complex was laid down onto functionalized electrodes, such as ITO, Au and SiO2 electrodes modified with or without lipid bilayers. Upon illumination photocurrents were successfully measured. Excitation spectra confirmed that these photocurrents was produced by light absorbed by the pigment-protein complexes as shown in our previous data (M. Ogawa, M. Nango, et.al., *Chem. Lett.*, 772-773 (2004) and M. Kondo, M. Nango, *Biomacromolecules*, **8**, 2457-2463 (2007), A.Sumino M. Nango, et.al., *Langmuir*, **27**, 1092-11099 (2011)) .

It proved critical in these studies to capitalize on our knowledge of the behavior of these complexes to

select those that are the most stable and well organized. The best results was only obtained with the subset of the most stable complexes, the combination of LHCII and PS II-Histag on Au electrode as well as the combination of LH2-SH and C-Histag LH1-RC assembly onto SiO2 and Au, respectively which the orientation and direction of these complexes are controlled. These studies was examined to correlate the supramolecular organization of the complexes on the electrodes with an efficient capture of photons.

AFM and EM studies resolved the organization of antenna complexes both in reconstituted lipid bilayers and in native photosynthetic membranes. These techniques are now being applied to investigate the organization of the antenna complexes and their synthetic model complexes on the electrodes. This work required very careful attention to detail and the current pictures are very exciting.

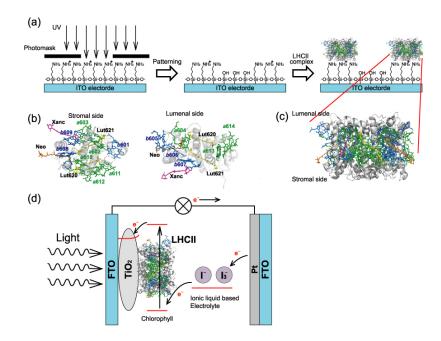


Scheme 4 Schematic model of the assembly of photosynthetic pigment complex (LHCII,PSII and PSI) with pigments on various substrates with pattern.

Task 2: Preparation of photo-volatic biosolar cells using the antenna complexes such as FCP from algae and LHCII from plant (Ref. 7: ACS Macro Lett., 1, 296–299(2012))

A light-harvesting (LH) antenna complex II, LHCII, isolated from spinach was immobilized onto an ITO electrode with dot patterning of 3-aminopropyltriethoxysilane (APS) by utilizing electrostatic interactions between the cationic surface of the electrode and the anionic surface of stromal side—of—the LHCII polypeptideas shown in Scheme 5. Preparations of—fluorescence with pattern and photo-volatic biosolar cells using antenna complexes such as FCP and LHCII were accomplished, allowing them to work under dim or diffuse light. Figure 1 shows that illumination of LHCII assembled onto the ITO electrode produced a photocurrent response that depends on the wavelength of the excitation light. The photocurrent action spectrum was reasonably consistent with the absorption spectrum of LHCII, indicating chlorophyll a clusters on the stromal chlorophylls play an important role on the photocurrent activity. Further, FCP as well as LHCII was immobilized onto a TiO₂ nano-structured film to extend for development of dye-sensitized biosolar cell system as

shown in Scheme 5d). Interestingly, the photocurrent measured in the iodide/tri-iodide redox system of an ionic liquid based electrolyte on the TiO₂ system showed remarkable enhancement of the conversion efficiency, as compared to that on the ITO electrode (Table 1).



Scheme 5. (a) Schematic model of assembly of LHCII complex (PDB; 1rwt) on ITO electrode modified with APS pattern. (b) Pigment location in LHCII monomer at Lumenal and Stromal sides. Green, Chl *a*; blue, Chl *b*; yellow, lutein; orange, neoxanthin; magenta, xanthophylls-cycle carotenoids. (c) Side view of LHCII trimer. (d) Schematic model of the DSSC (Dye Sensitized Solar Cells) using LHCII immobilized onto a TiO₂/FTO electrode.

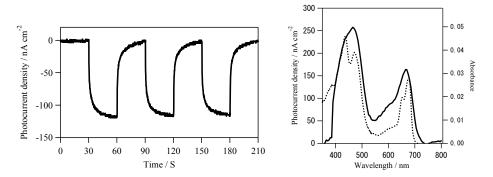


Figure 1. (a) Photocurrent response of LHCII assembled on an APS-ITO electrode in buffer solution when illuminated at 670 nm. (b) Action spectrum of LHCII assembled on an APS-ITO electrode (solid line) and the absorption spectrum of LHCII in aqueous solution (dotted line).

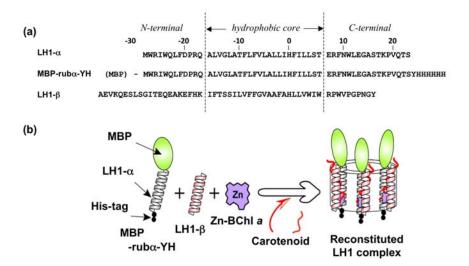
Table 1 Performance characteristics of DSSC based on FCP and LHCII

	Voc (V)	Jsc (mA/cm ²)	FF	η (%)
LHCII	0.57	0.48	0.58	0.16
FCP	0.64	0.43	0.37	0.10

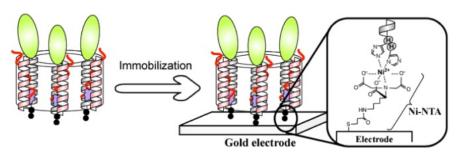
2. Artificial assembly of synthetic LH model polypeptides with pigments on various electrodes.

Task 3: Reconstitution and organization of photosynthetic antenna model protein complex bearing functional hydrophilic domains (Ref. 2 & 3: *Chem. Lett.*, 40, 1280-1282 (2011) & *Photosynthesis Res.*. 111,63-69(2012))

Bacterial photosynthetic antenna polypeptide (LH) was synthesized as a water-soluble fusion protein with maltose-binding protein (MBP) and a His-tag portion (MBP-rubα-YH) using an *E. coli* expression system(Scheme 6(a)). Reconstitution experiments indicated that LH-type complexes with pigments were successfully formed(Scheme 6 (b), regardless of the presence of a large hydrophilic MBP portion. The reconstituted complex was immobilized onto a Au electrode via a His-tag-Ni-NTA interaction as shown in Scheme 7. Figure 2 showed that when the complex was incorporated into a planar lipid bilayer, protruding MBP portions were clearly observed by AFM.



Scheme 6. (a) Amino acid sequences of native *Rsp. rubrum* LH1-α, LH1-β peptides, and MBP-rubα-YH. (b) Reconstitution of the LH1 complex using MBP-rubα-YH, LH1-β, Zn-BChl *a*, and a carotenoid (spirilloxanthin, spx, or spheroidene, sphe).



Scheme 7. Immobilization of the MBP-modified reconstituted LH1 complex on a Ni-NTA-modified Au electrode.

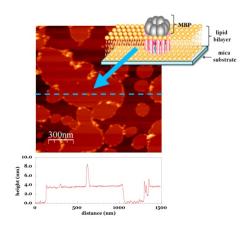


Figure 2. AFM image of reconstituted LH1-complex Assembly

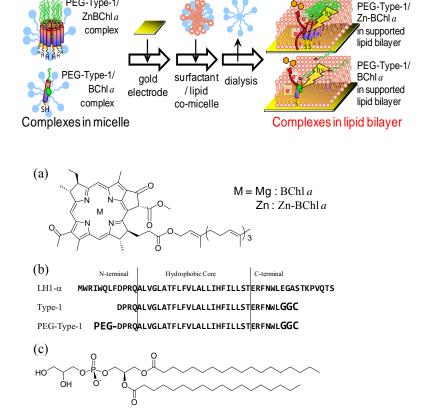
Taken together, the results of this study suggest that the genetically engineered MBP-rub α -YH is useful for construction of artificial photosynthetic antenna systems based on the promising methodology using functional hydrophilic domains, His-tag and MBP for immobilization onto electrodes with a defined orientation and as a molecular landmark for AFM observation at the molecular level, respectively.

Task 4: Two-dimensional molecular assembly of chemically synthesized LH model polypeptides with photosynthetic pigments on electrodes (Ref.6 : ACS MacroLett., 1, 28-22(2012))

The two-dimensional molecular assembly was accomplished of BChl a and Zn-BChl a together with synthetic PEG-linked LH model polypeptides on a gold Au(111) electrode modified with supported lipid bilayers as shown in Scheme 8. Model polypeptides for LH1- α were successfully synthesized and stablyassembled with Zn-BChl a in lipid bilayers on an electrode. The PEG moiety of the model polypeptide assisted the stable assembly with an α -helical conformation of the LH1- α model peptides together with these pigments onto the gold electrode with defined orientation. Figure 3 shows the cathodic photocurrent responses and schematic diagrams of electron transfer. The photocurrent response depended on the combinations of the pigments and synthetic LH model polypeptides. Interestingly, increased photocurrent for the co-assembly of PEG-Type 1/ BChl a and PEG-Type 1/ Zn-BChl a on the substrate

implies due to energy transfer from Bhl a complex to Zn-BChl a complex was observed. The results presented herein was useful for the self-assembly of these complexes on electrodes to construct efficient energy-transfer and electron-transfer reactions between individual pigments in lipid bilayers.

This method will be useful for the self-assembly of these complexes in order to study the energy transfer and electron transfer reactions (capture of photons) between individual pigments in the supra-molecular complexes on the electrode with supported bilayers as well as to provide insight into the effect of the structure of 1α -helix hydrophobic polypeptide on the energy transfer and capture of photons.



PEG-Type-1/

Scheme 8. Schematic model of the two-dimensional assembly of poly(ethyleneglycol) (PEG)-linked synthetic LH model polypeptides with pigments on a Au electrode with supported lipid bilayers. (a) Zn porphyrin pigments, (b) Amino acid sequences of synthetic 1α-helix hydrophobic polypeptide, (c) The structure of lipid

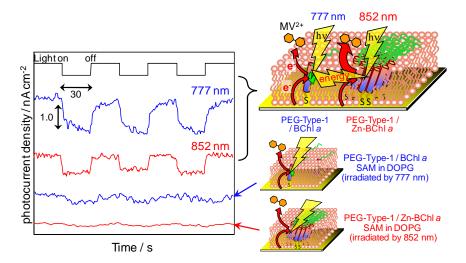


Figure 3. Cathodic photocurrent responses and schematic diagrams of electron transfer

Pay-off

Effects of dissemination of research results are as follows,

- 1) Assembly of photosynthetic antennas and their protein-mimic complexes on electrodes with nanopattern. This proposal aims to incorporate modified core complex (PSII and PSII) and the antenna (LHCII) complexes, and their model complexes onto Au, ITO and SiO2 with pattern. If this trial becomes successful, it can trigger the development of a new information technology, IT industry as well as development of a new new type of nano-photonic sensors and nano-semiconductors..
- 2) Efficient usage of light energy. Photosynthetic antennas can collect light energy in the entire region from ultraviolet to near infrared. It has a unique property to harvest a small number of photons from all the different directions and to concentrate them for usage. This mechanism to enable high sensitivity in a wide spectral region can be used as a guiding principle in designing photo-electronic materials.
- **3) Key to solve the energy and environmental crisis.** Development of a safe and economical system for conversion of light energy into electricity is crucial in order to solve the energy and environmental crisis. The photosynthetic system is a best refined material in harmony with the global environment, and the present project aims to create a novel battery or sensors for the next generation using the solar energy which is exhaustible, clear and free of pollutant.

Summary

The present generations of sensor and semiconductor devices with an integrated circuit for developing nano-level size are too expensive to be cost-effective compared to other existing technologies. Expanding existing silicon device technologies and nanofabrication technics by incorporation of modified photosynthetic protein / pigments complexes such as PSI, PSII, FCP and LHCII from algae and plants or their protein-mimic materials to perform tasks of light-harvesting and charge separation, is currently explored as a novel concept, which makes use of natural protein environments to create a directional flow of light energy and electronic charge separation, meanwhile reducing the cost aspect by the use of bio-materials and their synthetic protein-mimic materials. Based on biological design principles, future biology-based photonics or their synthetic organic photonics could

form clean and inexpensive future alternatives for productions of nano-sensors and nano-semiconductors.

We proposed a scenario where construction of artificial photosynthetic systems with patterning substrate is expected to start from molecular and supra-molecular entities in a variety of smart matrices that collect light energy and separate charge, leading to an electrochemical potential that can be used to produce current for developing new types of nano-biophotonics

4.List of Publications:

A. Journal Paper publication:

- 1. A. Sumino, T. Dewa, T. Takeuchi, R. Sugiura, N. Sasaki, N. Misawa, R. Tero, T. Urisu, A. T. Gardiner, R. J. Cogdell, H. Hashimoto, M. Nango, "Construction and Structural Analysis of Tethered Lipid Bilayer Containing Photosynthetic Antenna Proteins for Functional Analysis", *Biomacromolecules*, **12**, 2850-2858 (2011). (Doi:org/10.1021/bm200585y)
- 2. S. Sakai, A. Hiro, A. Sumino, T. Mizuno, T. Tanaka, H. Hashimoto, T. Dewa, M. Nango, "Reconstitution and Organization of Photosynthetic Antenna Protein Complex Bearing Functional Hydrophilic Domains", *Chem. Lett.*, **40**, 1280-1282 (2011). (Doi:10.1246/cl.2011.1280)
- 3. S. Sakai, A. Hiro, M. Kondo, T. Mizuno, T. Tanaka, T. Dewa, M. Nango, "Overexpression of *Rhodobacter sphaeroides* PufX-bearing maltose-binding protein and its effect on the stability of reconstituted light-harvesting core antenna complex", *Photosynthesis Res.*.
- **111**,63-69(2012)(Doi:10.1007/s11120-011-9673-x)
- 4. D. Uchiyama, H. Hoshino, K. Otomo, T. Kato, K. Onda, A. Watanabe, H. Oikawa, S. Fujiyoshi, M. Matsushita, M. Nango, N. Watanabe, A. Sumino, T. Dewa, "Single-protein study of photoresistance of pigment-protein complex in lipid bilayer", *Chem. Phys. Lett.*, **511**, 135-137 (2011).(10.1016/j.cplett.2011.06.019)
- 5. D. Uchiyama, H. Oikawa, K. Otomo, M. Nango, T. Dewa, S. Fujiyoshia, M. Matsushita "Reconstitution of bacterial photosynthetic unit in lipid bilayer studied by single-molecule spectroscopy at 5 K" *Phys. Chem. Chem. Phys.*, **13**, 11615-11619 (2011).(Doi:10.1039/c1cp20172g) 6. T. Ochiai, M. Nagata, K. Shimoyama, T. Kato, T. Asaoka, M. Kondo, T. Dewa, K. Yamashita, A. Kashiwada, S. Futaki, H. Hashimoto, M. Nango, "Two-Dimensional Molecular Assembly of Bacteriochlorophyll a Derivatives Using Synthetic Poly(Ethylene Glycol)-Linked Light-Harvesting Model Polypeptides on a Gold Electrode Modified with Supported Lipid Bilayers", ACS Macro Lett., **1**, 28-22(2012). (Doi: org/10.1021/mz200048m)
- 7. M. Nagata, M. Amano, T.Joke, K. Fuji, A. Okuda, M. Kondo, S.Ishigure, T. Dewa, K. Iida, F. Secundo, Y. Amao, H.Hashimoto, M. Nango, Immobilization and Photocurrent Activity of a Light-Harvesting Antenna Complex II, LHCII Isolated from a Plant on Electrodes, *ACS Macro Lett.*, 1, 296–299(2012). (Doi: org/10.1021/mz200163e)

8. M. Kondo, K. Iida, T. Dewa, H. Tanaka, T. Ogawa, S. Nagashima, K. V. P. Nagashima, K.Shimada, H. Hashimoto, A. T. Gardiner, R. J. Cogdell, M. Nango, "Photocurrent and Electronic Activities of Oriented-His-tagged Photosynthetic Light-Harvesting/Reaction Centre Core Complexes Assembled onto a Gold Electrode", *Biomacromolecules*, 13, 432–438(2012) (Doi: org/10.1021/bm201457s) 9. M. Kondo, T. Dewa, M. Nango, "Assembly of Photosynthetic Pigment-Protein Complex on Substrates and Development of Bio-solar cell", *Bioindustry*, 29, 18-26 (2012).

B.Conference presentations (International conference):

1. M. Nango, M. Kondo, T. Dewa, H. Hashimoto, "Artificial Photosynthetic Antenna: Self-Assemblies of Light-Harvesting Protein-Pigment Complex and Its Model Complex for Construction of an Artificial Photoenergy Conversion System", 2011 Korean-Japan Bilateral Symposium on Frontier Photoscience

Abstracts

At the early stages of purple bacterial light-harvesting complexes, light-harvesting complexes, called LH1 and LH2, absorb solar energy and transfer it to the reaction center (RC), whereupon the absorbed energy is efficiently converted into electrochemical energy. These reactions take place within a 'core complex' consisting of a RC located inside the LH1 complex, where porphyrin complexes play important roles on these reactions. We are interested in the rapid and efficient energy transfer between porphyrins in these complexes(1-5). Porphyrin complexes have been aiming to construct an artificial solar energy device based on a natural solar energy conversion system such as the core complex. The X-ray crystal structure of the LH1-RC core complex has been reported and revealed that it is oval rather than circular. The core complex, isolated from the photosynthetic bacterium, Rps. palustris, was successfully assembled onto an Au electrode modified with various terminated alkanethiol by using an electrostatic interaction (3). Efficient energy transfer and photocurrent responses of the complexes were observed upon illumination at 880 nm. Interestingly, the fluorescence of bacteriochlorophyll a (BChl a) molecules in the LH complex was strongly quenched due to the presence of RC when illuminated at 880 nm, implying that an efficient energy transfer from BChl a in the LH1 complex to RC in the core complex occurred. Furthermore, the photocurrent generated from the core complex assembled onto an Au electrode depended on the wavelength of the exciting light (Figure 2b). This action spectrum revealed a maximum at the wavelength corresponding to the absorption band of the complex. At this wavelength an enhanced photocurrent was observed for the core complex of Rps. *palustris* compared with that of *R. rubrum*.

An enhanced photocurrent was also observed in the case of LH 1 model polypeptides assembled with porphyrin derivatives onto an Au electrode (6). In this case the photocurrent response depended on the structure of the model complex. Various combinations of these complexes are being tested for their usefulness in constructing artificial solar energy conversion devices.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) and AOARD (FA2386-11-1-4068).

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